

"IN SITU" OBSERVATIONS OF LIQUID DIFFUSION IN THIN SECTIONS OF COAL

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INTRODUCTION

The objectives of this study are to advance our understanding of how liquids penetrate through the microstructure of coals and to use diffusion to probe the macromolecular and microstructure of coals. Diffusion of liquids and of solids dissolved in liquids is of considerable importance in many areas of coal technology and science. Many coal liquefaction processes involve the penetration of a liquid into coal; in particular, this is the case for many slurry-based liquefaction processes. There are a number of coal beneficiation processes actively being investigated which rely on diffusion of reagents into the coal to modify its structure or to remove undesired mineral or organic components. Similarly, many chemical pretreatments of coals depend on diffusion for the reagents to reach the reactive sites in the coal. Mass transfer is crucial to many fundamental chemical investigations of coal structure which utilize wet chemical techniques since reagents must diffuse to reactive sites within the structure. From a fundamental viewpoint a better understanding of diffusion in coal will advance our overall comprehension of the underlying macromolecular structure and microstructure of coals.

The escape of reaction products, mobile coal molecules, or molecular fragments from the coal structure are other diffusional processes in coal which are of substantial technological importance. For example, they occur in most conversion processes. In liquefaction, liquids or gases produced within the coal or molecular fragments of the coal dissolved in the liquids must escape from within the coal particles. In gasification molecular fragments from the degraded coal structure must diffuse to the surface of the particle before they can evaporate into the surrounding gas.

In this study we focus on a reasonably well-defined system in order to better understand diffusion phenomenon. We investigate the diffusion of good liquid swelling agents into a high volatile bituminous coal. Since the diffusing swelling agents greatly enhance the mobility of the macromolecular chain segments within the coal, this system is particularly well suited for probing macromolecular aspects of the coal structure.

The diffusion of liquids in materials is commonly studied by fluid uptake and/or desorption as a function of time. For simple or well-behaved materials this approach is effective, but for coal which is highly heterogeneous varying markedly from sample to sample and from micro-region to micro-region within each sample, this approach can give only averaged and incomplete information. A technique utilized with polymers is to characterize diffusion by observing the movement of colored solvents, liquids colored with dyes, or index of refraction gradients in the material. These methods have not been successfully applied to coals because of the high opacity of coals and the difficulty in fabricating satisfactory samples.

In this study we report the first successful "in situ" microscopic observations of diffusion in coals. The techniques involved first producing uncontaminated thin section specimens of coals using methods developed in our laboratory. Then special procedures were developed for securing the specimen, shielding the top and bottom surfaces from the penetrant and exposing the edge of the thin section to the selected solvent. This technique enables one to follow the kinetics of the diffusion in detail under the microscope in transmitted light as the solvent penetrates the coal. In this manner the maceral composition, mineral matter, and other aspects of the microstructure are observed directly during the diffusion process, and the heterogeneity of the coal can be accounted for

explicitly. This is crucial to the understanding of the diffusion phenomenon in coals since for adequate evaluation it is necessary to be able to measure the progress of the solvent into each of the micro-components which are being penetrated within the coal.

EXPERIMENTAL

The coal used in these studies was Illinois No. 6 from the Monterey No. 1 mine which is of high volatile C bituminous rank. Because coal is so highly absorbing in the visible region of the spectrum, transmitted light optical microscopy can only be done with very thin specimens. Unfortunately, coal is a fragile material in thin pieces and it readily breaks into small fragments. For this reason special techniques must be used to prepare the thin section specimens. To avoid fragmentation of the thin slivers of coal, the specimens are normally embedded in an adhesive cement such as an epoxy adhesive. However, the diffusional characteristics of such embedded specimens are affected by the adhesives, so they are not satisfactory for diffusion studies. Canada Balsam has been used by many investigators as a securing agent for the coal. It can be mostly removed, but it leaves behind residues which are undesirable contaminants in the coal and may affect diffusion in unpredictable ways. The sample preparation procedure used to prepare the samples for this study utilized an adhesive which is completely soluble. The adhesive is a paraffin-based embedding wax (1). It is soluble in hexane which has a minimal effect on the coal. This sample preparation procedure has been described previously (2) and will not be described further here. The samples were cut perpendicular to the bedding plane. The thin sections were about 15 micrometers thick and roughly 0.5 mm across.

All of the experiments described in this paper were at room temperature and atmospheric pressure. The diffusing liquid used in this study was reagent grade pyridine.

Once satisfactory thin section specimens have been prepared they cannot simply be immersed in the solvent. If the whole surface of the sample were exposed to the solvent, then penetration would occur from all sides and the specimen would be rapidly penetrated in its thin direction from solvent coming through the top and bottom. The kinetics of this process would be difficult to interpret and even more difficult to quantify. Rather, it is desirable to prevent the solvent from penetrating through the top or bottom of the thin section and to allow it to penetrate only from one edge. Unfortunately, because of the tiny size and delicate character of the specimens one can not simply dip one edge of the sample in the solvent.

Two different techniques for holding the thin section samples and exposing them to the penetrating liquid were developed. Each of the techniques has advantages and disadvantages depending on the particular type of information which most interests the investigator. In the "grease-immersion" technique the solvent is prevented from contacting most of the top and bottom surfaces of the thin section by coating most of these surfaces with a grease. The grease must itself be an adequate barrier to the solvent. Some of the materials which were found usable were fluorinated greases (3) and a low molecular weight uncrosslinked butyl rubber (4). A small area of the top and bottom surfaces is left uncoated to avoid getting grease on the edge. The thin section is then placed between two glass slides. A schematic diagram of the grease-immersion setup is shown in Figure 1. At the start of the experiment a drop of liquid solvent is placed in contact with the uncoated edge of the thin section. The liquid then penetrates through one edge and propagates into the thin section of coal parallel to the surface.

In the weighted coverglass method the thin section of coal is sandwiched between a 1 mm thick glass slide on the bottom and a No. 1-1/2 glass coverslip on top. Weights are put along the edges of the coverslip so that good contact between the coal and the glass surfaces is insured. While it might be thought that the solvent would very rapidly wick along the glass surfaces and thereby quickly penetrate the coal from the top and bottom surfaces, this did not tend to occur in practice. Apparently, where the solvent does penetrate in between the glass and the

top or bottom of the thin section, the coal swells. This swelling effectively plugs up the channels where the solvent was penetrating -- right where the plug was needed. Additionally, where the solvent penetrated along the surface of the coal, it transformed the surface coal material into a rubbery state. The rubbery surface-coal acted as a gasket preventing any appreciable further penetration by the solvent.

During a diffusion experiment the solvent can not be directly observed within the coal because it is transparent. Rather, the swelling caused by imbibition of the solvent renders the diffusion observable. When the solvent swells the coal it appears to be a lighter color. This lighter color occurs primarily because for the swollen coal there is less material per unit cross sectional area of the coal in the path of the light passing through the sample. There may also be an effect caused by the change in index of refraction of the pore space as it becomes filled with fluid, but this effect is far less than from swelling for the pyridine-Illinois No. 6 coal system.

An "in situ" diffusion experiment was started by bringing a drop of solvent into contact with the edge of the coal thin section which was properly set-up as described in the previous section. The time of liquid contact was recorded and the sample was observed on the microscope stage in transmitted light. Periodically photomicrographs were taken and the time was noted in order to record the kinetics of the process. The liquid was kept in contact with the edge of the coal throughout the experiment.

RESULTS AND DISCUSSION

Diffusion of Pyridine in relatively homogeneous vitrinite

A thin section sample of Illinois No. 6 coal consisting of relatively homogeneous vitrinite was used for a diffusion experiment. The sample was placed in the grease-immersion setup. Liquid pyridine was brought into contact with the exposed edge of the sample. The thin section was then observed in the microscope as the liquid penetrated into the edge of the sample and diffused into the coal parallel to the surface of the thin section. Figure 2 shows the sample after 50 minutes exposure to the pyridine. The circle of light on the sample is caused by the field diaphragm of the microscope which is partially closed to keep light from passing around the sides of the sample. Illuminator light which does not pass through the coal is very bright and the haze caused by it tends to obscure the more dimly illuminated structural features of the coal. In Figure 2 a very abrupt change in coloration at the diffusion front is evident. Just ahead of the diffusion front the coal is the dark red color of the unchanged coal whereas just behind the front the coal is a much lighter orange-yellow color. This sharp diffusion front having an abrupt change in penetrant concentration demonstrates that the diffusion of the liquid in the coal is highly concentration dependent. A strong concentration dependence is characteristic of many macromolecular materials, especially in cases where the imbibition of the liquid transforms the macromolecular substance from a glassy material to a rubbery or viscous state and/or where the solvent swells the sample. In the coal behind the diffusion front where the solvent has already penetrated to an appreciable concentration there is relatively little change in the color of the coal. Since the color of the coal is related to its degree of swelling or the concentration of imbibed solvent, it is seen that there is relatively little change in the concentration of the solvent in the coal behind the diffusion front.

There are several particular modes of diffusion which could cause the very abrupt change in solvent concentration at the diffusion front along with the small change in solvent concentration behind the front. For example, a system where some of the penetrant can react with the matrix and the reaction is faster than the diffusion, can exhibit a relatively sharp front. Also, a relatively sharp front will result from a Fickian diffusion coefficient which is small at low concentrations of penetrant, but which abruptly jumps up to a much larger value at some concentration.

We had demonstrated previously (5) that swelling of this coal with pyridine depresses the glass transition temperature of the coal below room temperature and transforms it into a rubbery state. For polymers, when a liquid plasticizes it to above its glass transition, the diffusion is sometimes of Case II type (6). Case II is the name given to diffusion which has the following characteristics (7). There is a very sharp diffusion front. The diffusion front propagates into the material at constant velocity. And, there is extremely small variation in the concentration of the penetrant in the region behind the diffusion front. We have shown that the diffusion of pyridine into vitrinite in Illinois No. 6 coal has the first and last of these characteristics. The velocity of movement of the diffusion front will be discussed later.

The diffusion front in Figure 2 has substantial curvature and is somewhat irregular. The curvature may be caused by the exterior geometry of the sample and/or the shape of the region where the liquid pyridine contacts the coal. The irregularity of the diffusion front is caused by the micro-heterogeneity of the vitrinite -- even though it appeared relatively homogeneous under the microscope.

Large regions of variable coloration are seen trailing behind the diffusion front in Figure 2. The pattern of the coloration suggests that it is caused by strains in these flexible regions of the sample behind the diffusion front which are restricting solvent uptake. Such strains might be caused by stresses resulting from the swelling, which is highly anisotropic in the vicinity of the diffusion front. Strains could also have been caused by deformation of the coal at some earlier stage in its evolution. Another possibility is that this coloration comes from regions having variable composition which results in a variable rate of swelling. However, the relationship between these regions of variable color and the position of the diffusion front makes it most likely that this behavior is a direct consequence of the diffusion and/or the resultant swelling.

The diffusion front is somewhat ragged, but it is not grossly irregular. There are bits of unswollen vitrinite just behind the front. There is a prominent "finger" of vitrinite which has not yet been swollen by the pyridine; however, there are some channels of swollen material in it which have been penetrated by the pyridine. This finger of vitrinite clearly must be appreciably different from the surrounding vitrinite.

Figure 3 shows the sample after 78 minutes exposure to the pyridine. The shape of the diffusion front has changed considerably. It is seen that the finger of Figure 2 has been completely penetrated by the pyridine and is now indistinguishable from the surrounding vitrinite. It is also seen that the small bits of unpenetrated vitrinite behind the front in Figure 2 have been penetrated and swollen. It was observed that when these small regions begin to change to a lighter color in one part they then tend to change relatively quickly to the lighter color overall. It appears as if there is some sort of barrier to the solvent surrounding these small regions, perhaps a membrane or coating. Then, once the barrier becomes penetrated by the solvent the whole inside is relatively rapidly penetrated. It is clear from these photographs that the "homogeneous-appearing" vitrinite is far from homogeneous, but rather there is considerable variation from region to region within it.

A potential difficulty with the grease-immersion technique used in this experiment is that transfer of solvent either into or out of the top or bottom surfaces of the thin section may occur via the grease. The greases utilized were selected to minimize this effect. In addition, during the "in situ" experiment the sample was carefully monitored for evidence of appreciable solvent transfer through the grease. For example, appreciable direct transfer of solvent from the liquid reservoir through the grease to the coal would be expected to produce thin solvent-swollen regions along the edges of the sample, or at least to perturb the solvent concentration at the junction of the diffusion front with the edge of the sample. No evidence of either of these effects was observed. However, an estimate of the magnitude of loss or gain of solvent through the grease would be desirable to reliably evaluate its effect on the kinetics of the diffusion process.

When the sample was observed through the optical microscope in transmitted light between crossed polarizers, a thin, orange-colored line stood out against the

darkened thin section. With time, this thin line moved further into the sample. When the polarizers were removed, it was seen that the thin orange line corresponded to the position of the diffusion front; that is, it occurred at the position where the color of the coal changed from the dark red color of the unswollen coal to the light orange color of the expanded coal. The thin orange-colored line which is observed between crossed polarizers at the position of the diffusion front is apparently caused by the orientation of the coal structure in this region. The expanding coal behind the diffusion front is constrained by the unswollen coal ahead of the diffusion front. This can be expected to stretch and align the macromolecular network in this region. Such partially oriented macromolecular chains cause a significant difference in the index of refraction parallel and perpendicular to the direction of orientation. This causes a rotation in the direction of polarization of light passing through the specimen. The result is that some light passes through the second of the crossed polarizers. A short distance behind the diffusion front there is enough flexibility that the macromolecular orientation is diminished and the orange line is no longer seen. The orientation of the structure in the region of the diffusion front and the relaxation of the orientation behind the front are further evidence for the macromolecular nature of the coal and the transition of the coal from a rigid to a rubbery material.

Diffusion of pyridine in coal having a heterogeneous striated structure

A thin section of Illinois No. 6 coal having a heterogeneous striated structure was used in a diffusion experiment. The sample was about 15 micrometers thick and, as in the other samples, its surface was perpendicular to the bedding plane. Figure 4 shows the sample after its edge has been in contact with liquid pyridine for 4 minutes. The dark gray material seen in the photomicrograph is the vitrinite or wood-derived component of the coal. In this sample it is seen to occur as strands which are approximately parallel to the bedding plane. The bedding plane is seen edge-on in the photograph. The lighter bits of material are the liptinite which is the more hydrocarbon-rich waxy component. This component is derived from non-woody parts of plants such as spores, pollen, and stem and leaf coatings.

A sharp diffusion front is seen in Figure 4. The front is similar to that seen in the homogeneous vitrinite sample of Figure 2. The front here, though, is more ragged because of the different macerals present in the sample. It is also seen that some of the vitrinite strands behind the diffusion front are far more darkly colored than the other vitrinite behind the front. Apparently these particular vitrinite macerals are more slowly penetrated by the pyridine. In time, though, these macerals are penetrated and swollen and become light-colored.

Figure 5 shows the sample after 52 minutes exposure to pyridine. Although the coal specimen in Figure 5 is quite heterogeneous, the diffusion front is not far from being straight. There are, however, a number of small fragments of vitrinite behind the front which appear to be very slightly, if at all, penetrated by the pyridine. These bits of vitrinite may have a coating or membrane surrounding them which retards penetration by the pyridine, or this material may have a less permeable structure which the pyridine penetrates more slowly. However, with time almost all of these darker fragments behind the diffusion front are swollen and become light-colored. It is also evident from comparing Figures 4 and 5 that there has been substantial swelling in the pyridine of the large liptinite maceral in the left center of the photomicrograph.

Diffusion rates parallel and perpendicular to the bedding plane

In order to compare the diffusion rates of the solvent parallel and perpendicular to the bedding plane of the coal all four edges of a thin section were simultaneously exposed to the pyridine. This sample had a striated structure. Its surface was perpendicular to the bedding plane; the bands of material ran parallel to the bedding plane and the direction perpendicular to the bands was perpendicular to the bedding plane. Figure 6 shows this thin section after 15 minutes in contact

with the liquid pyridine. It is seen that the penetration rates of the pyridine in the directions parallel and perpendicular to the bedding plane are comparable.

Some investigators have reported that the diffusion rates of various fluids in coals is much faster parallel to the bedding plane than perpendicular (8,9). An important difference between these prior investigations and our current studies is that we are observing primarily intra-maceral diffusion whereas earlier work was more effected by larger scale diffusion. We showed earlier (9) that major routes for rapid penetration of the coal structure included intermaceral interfaces, cracks, holes, and regions containing mineral matter accumulations. These types of irregular regions within the coal tend to extend along the bedding plane. Therefore, on a large scale faster diffusion can be expected parallel to the bedding plane. Our studies however, are more concerned with the finer structures of the coal. We have focused on the diffusional behavior within individual vitrinite macerals within the coal. Within the individual macerals or for groups of macerals which are in intimate contact with each other and which do not contain substantial irregular regions, the diffusion rates parallel and perpendicular to the bedding plane are comparable.

Self-sealing in coal undergoing solvent-swelling

A thin section sample of vitrinite was exposed to pyridine using the weighted coverglass method. In Figure 7, the sample is shown after 60 seconds contact with the pyridine. Note the lightened areas indicating solvent penetration and solvent swelling along the edges of the large crack in the sample as well as along the edges of the sample. The sample is shown in Figure 8 after 100 seconds exposure to the pyridine. Note that the large crack has fully closed. Also, whereas the diffusion front has moved substantially in from the outer edges of the sample there has been relatively little movement of the diffusion front along the edges of what was the large crack. Figure 9 shows the sample after a total of 210 seconds exposure to the pyridine. There has been considerable additional movement of the diffusion front into the coal from the edges. However, along what was the large crack there has been little change in the coal.

These observations illustrate one important mechanism which can occur during the diffusion of good swelling solvents into coals. The swelling of the coal may seal-off cracks and holes in the coal and thereby stop or diminish penetration of the solvent through these routes. Although such routes may constitute a very small volume of the coal, if they were not sealed by the swelling they can be major routes for uptake of the solvent. For example, our prior work on diffusion of oxygen into coals (9) has shown that the cracks and holes provide paths for rapid penetration of oxygen into the interior of the coal.

The self-sealing effect may also have important consequences on the sub-microscopic scale. Pores within the coal, or inter-maceral interfaces in the coal which have previously been shown can be routes for rapid penetration by fluids (9) may be sealed by swelling if the solvent starts to penetrate them. On the other hand, porosity within mineral matter accumulations is less likely to be plugged by swelling (unless there is a substantial concentration of swellable organic matter within the region of mineral matter. Note, however, that the sealing mechanism is only expected to be operable in localized regions which swell in advance of surrounding materials. If all of a region swells isotropically, then cracks and holes in the region will also swell and sealing will not occur. It should be kept in mind, however, that the converse of self-sealing frequently occurs; that is, stresses produced during solvent swelling often produce cracks in coal particles (10).

Kinetics of Diffusion and Re-diffusion

The movement of diffusion fronts as they penetrated into thin section specimens was quantified for several samples. For each sample the rate of propagation of the diffusion front into the sample was quantified. The results were somewhat variable, probably because of the heterogeneous nature of the coal. For

all samples measured, though, there was a pronounced slowing down of the velocity of the diffusion front with increasing time, as the front penetrated deeper into the sample. This would suggest that the diffusion is not Case II. However, because the amount of solvent penetrating through the grease, or between the glass slide and the coal into the top and bottom surfaces of the coal has not been accurately quantified (though qualitative checks were made -- see earlier in this section), it would be desirable to corroborate these results either through an accurate evaluation of this contribution to solvent uptake or by using alternate techniques.

After the diffusion front had propagated well into the thin section, the pyridine was removed and the sample was allowed to dry at room temperature in nitrogen gas for several days. Then the same diffusion experiment as before was repeated. Figure 10 shows graphically the results for both the original diffusion and the second exposure after drying. It is evident that the movement of the diffusion front is much more rapid for the second run, after the sample has previously been swollen by the pyridine and dried. This faster diffusion in the second run had been observed in our previous work where thin sections were fully immersed in liquid pyridine and penetration occurred primarily through the top and bottom surfaces (11).

There are several possible contributions to the more rapid penetration of the pyridine the second time. When the sample is dried after the initial swelling, some of the pyridine remains in the coal (12). So, less pyridine diffuses into the coal the second time. In addition, the residual pyridine probably weakens some of the inter-molecular interactions so that the new pyridine diffusing in encounters a looser structure and can therefore swell the coal more readily. Another possibility is that the initial swelling and drying causes microcracks in the structure so that subsequent diffusion can utilize these new routes. However, in the regions where the diffusion rate was measured, no diffusion via microcracks was observable in the optical microscope. There may also have been some effect on the diffusion rate from some bitumen being extracted from the coal during the first diffusion run.

CONCLUSIONS

Diffusion into coal has been observed "in situ" at the microscopic level for the first time. This technique which utilizes uncontaminated thin sections of coal enabled the study of true intra-maceral diffusion as distinguished from the usual concurrent diffusion in a variety of maceral structures, or diffusion via cracks, mineral matter, macropores, or maceral interfaces. For diffusion of a good solvent into a high volatile bituminous coal, a sharply defined front occurred, and the diffusive flow was highly concentration dependent. The movement of the front slowed with depth of penetration into the coal. When the sample was placed between crossed polars, a thin light line was seen along the diffusion front against the dark background. This indicates that orientation of the macromolecular network occurs as a result of the stresses in the vicinity of the front. For intra-maceral diffusion in vitrinite there was no obvious difference between the rates of movement of the front parallel versus perpendicular to the bedding plane. When the liquid was desorbed and then reabsorbed, the diffusion rate was considerably faster the second time. Liquid penetration into cracks in vitrinite was initially rapid, but the swelling which resulted often sealed the cracks, greatly reducing further penetration.

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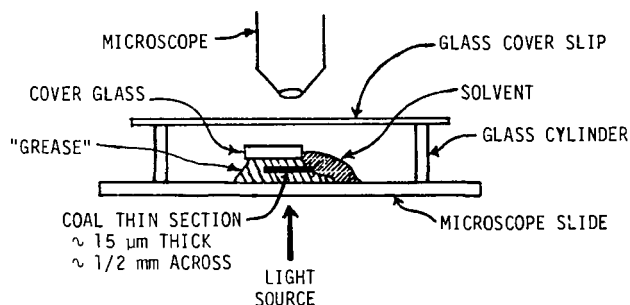


Figure 1. Grease-immersion setup for "in situ" microscopic observations of solvent diffusion in coals.



Figure 2. Diffusion of pyridine in relatively homogeneous vitrinite, after 50 minutes contact of edge with liquid pyridine.



Figure 3. Diffusion of pyridine in relatively homogeneous vitrinite, after 78 minutes contact of edge with liquid pyridine.



Figure 4. Diffusion of pyridine in a heterogeneous striated coal structure, after 4 minutes contact of edge with liquid pyridine.



Figure 5. Diffusion of pyridine in a heterogeneous striated coal structure, after 52 minutes contact of edge with liquid pyridine.



Figure 6. Comparison of diffusion rates parallel versus perpendicular to the bedding plane.

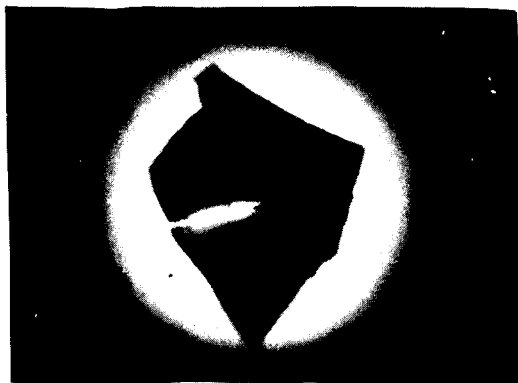


Figure 7. Thin section with crack, after 60 seconds exposure to pyridine.

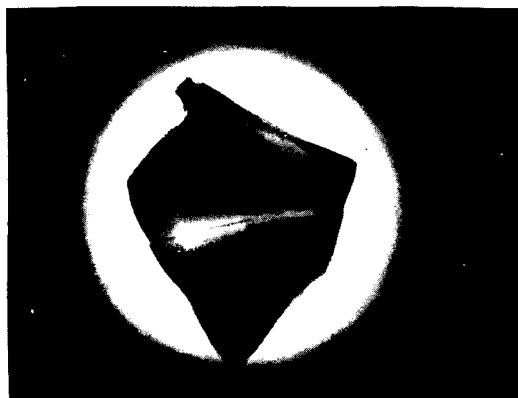


Figure 8. Crack in thin section sealed by swelling, after 100 seconds exposure to pyridine.



Figure 9. Thin section with sealed crack, after 210 seconds exposure to pyridine.

